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(54) Title: ADHESIVE COMPOSITIONS CONTAINING LOW MOLECULAR WEIGHT POLYPHENYLENE OXIDES**(57) Abstract**

Pressure sensitive and hot melt adhesive compositions having improved shear adhesion failure temperatures (SAFT) comprising: (a) a block copolymer having at least two monoalkenyl arene polymer endblocks (A) and at least one elastomeric conjugated-diene midblock (B), said blocks (A) comprising 8-55 % by weight of the block copolymer; (b) about 50 to about 200 phr of a tackifying resin compatible with block (B); and (c) about 5 to about 50 phr of a low molecular weight polyphenylene oxide polymer wherein the molecular weight (M_{vis}) of the polyphenylene oxide polymer is from about 1,000 to about 5,000, the T_g is from about 100° to about 165° C, preferably between 140-163° C.

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ADHESIVE COMPOSITIONS CONTAINING LOW MOLECULAR WEIGHT
POLYPHENEYLENE OXIDES

1 This is a continuation-in-part of copending U.S. Serial No.
2 355,532, filed May 23, 1989, entitled "Adhesive Composition
3 Containing Low Molecular Weight Polyphenylene Oxides," now
4 abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The invention relates to the use of low molecular weight
6 polyphenylene oxides in adhesive blends comprising styrenic triblock
7 copolymers such as polystyrene-polyisoprene-polystyrene (S-I-S) and
8 polystyrene-polybutadiene-polystyrene (S-B-S) to provide increases in
9 the shear adhesion failure temperatures (SAFT) of the corresponding
10 pressure sensitive, hot melt pressure sensitive or hot melt
11 adhesives. The SAFT increases are obtained without significant hot
12 melt formulation viscosity increases and with little impact on the
13 pressure sensitive adhesives' tack or peel strength.

2. Description of the Prior Art

14 In U.S. Patent 3,660,531, there are disclosed polyblends
15 containing: (A) greater than 50% of a thermoplastic resin matrix,
16 said resin matrix consisting of polyphenylene oxide resin in

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1 combination with alkenyl aromatic resins; and (B) less than 50% of an
2 elastomer selected from a group consisting of poly(butadiene), and
3 random, block or graft copolymers of butadiene and styrene. The
4 resulting blends exhibit unexpected thermoplastic properties
5 including improved melt processability and impact resistance without
6 sacrificing the desirable heat distortion temperature and flexural
7 modulus of unmodified polyphenylene oxide resin. The materials in
8 this patent are thermoplastic resins and not adhesives, and the
9 degree of polymerization (DP) of polyphenylene oxide is greater than
10 about 100.

11 Commonly assigned U.S. Patents 3,835,200 and 3,994,856
12 disclose respectively, polyphenylene ether and rubber styrene
13 copolymer compositions containing rigid block copolymers of
14 conjugated dienes and vinyl aromatic compounds, and high impact
15 rubber modified polystyrene compositions containing polyphenylene
16 ether and vinyl aromatic block copolymers; however, the compositions
17 are thermoplastics and the DP of the polyphenylene oxides is greater
18 than 50.

19 Hot melt adhesive compositions are disclosed in Hansen, U.S.
20 Patent 4,104,323. The adhesive composition is prepared by first melt
21 blending a polyphenylene ether resin and a low molecular weight
22 aromatic resin, and then blending the resulting mixture and a
23 monoalkenyl arene/conjugated diene block copolymer, tackifying resin,
24 and optional hydrocarbon processing oil. The molecular weight of the
25 polyphenylene oxide in the polyphenylene oxide alloy is between 6,000
26 and 25,000. The glass transition temperature is between 170 and
27 205°C. This melt blend avoids the use of solvents while also
28 avoiding oxidative degradation of the block copolymer. The resulting
29 polymer blend possesses a much higher service temperature when used
30 as an adhesive.

31 An adhesive composition having improved high temperature
32 properties is also disclosed in U.S. Patent 4,141,876. The
33 composition is prepared by melt blending a polyphenylene ether resin,
34 a selectively hydrogenated arene/conjugated diene block copolymer, a
35 tackifying resin, and optionally, a hydrocarbon processing oil. This

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1 patent is restricted to hydrogenated block copolymers which can
2 withstand the extremely high blending temperatures required to
3 disperse the polyphenylene oxide resins, (230°C to 260°C) and to
4 polyphenylene oxide resins having a molecular weight (M_{vis}) between
5 6,000 and 25,000. The glass transition temperature of the resin is
6 restricted to between 170° and 210°C.

SUMMARY OF THE INVENTION

7 A need exists in the practice of adhesive formulating to
8 obtain adhesive compositions with higher service temperatures and
9 manageable hot melt viscosities. The present invention describes the
10 use of low molecular weight polyphenylene oxide resins (PPO) in hot
11 melt or pressure sensitive adhesive compositions comprising:

12 (a) 100 phr of a block copolymer having at least two
13 monoalkenyl arene polymer endblocks A and at least one elastomeric
14 conjugated-diene midblock B, said blocks A comprising 8-55% by weight
15 of the block copolymer. Illustrative of the blocks are styrenic
16 block copolymers such as polystyrene-polybutadiene-polystyrene
17 (S-B-S), polystyrene-polyisoprene-polystyrene (S-I-S), poly
18 (α -methylstyrene)-polyisoprene-poly (α -methylstyrene), or their
19 selectively hydrogenated derivatives.

20 (b) about 50-200 phr (part per hundred rubber) of a
21 tackifying resin compatible with the rubbery midblock of the block
22 copolymers and

23 (c) about 5-50 phr of a low molecular weight PPO resin with
24 glass transition temperature (T_g) between 100°C and 165°C,
25 preferably between 140° and 163°C. ✓

26 The tackifying resin, which is compatible with the
27 elastomeric midblock of the triblock copolymer, is used to render the
28 formulation tacky. Preferred tackifying resins are those derived
29 from the copolymerization of diolefins and especially of C_5
30 diolefins such as piperylene with C_5 olefins such as
31 2-methyl-2-butene. These resins, such as ESCOREZ 1310LC, available
32 commercially from Exxon Chemical, have ring and ball softening points
33 between 80°C to 115°C. Another useful tackifying resin, Zonatac 105

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1 Lite, available from Arizona Chemicals, is prepared by the cationic
2 polymerization of limonene and styrene. Other useful tackifying
3 resins include those derived from rosin esters, terpenes, and terpene
4 phenolic resins. Hydrogenated versions of the above are also useful.

5 Hydrocarbon extending oils (0-200 phr) can be employed in
6 this application to modify the formulation viscosity and to increase
7 the tackiness of the adhesive. The extending oils, referred to as
8 paraffinic/naphthenic oils are fractions of refined petroleum
9 products having less than 30% by weight aromatics and viscosities
10 ranging from 100 to 500 SSU at 100°F. Oils are commercially
11 available such as Shellflex 371, a naphthenic oil manufactured by
12 Shell.

13 The adhesive formulations are prepared by dissolving in a
14 solvent such as toluene, and casting over a substrate such as mylar.
15 Optionally, to apply the formulation as a hot melt, the components
16 are melt blended in a Brabender mixer. The temperature for melt
17 blending will depend upon the T_g of the PPO. This is a significant
18 advantage of using PPO of lower T_g than that claimed in U.S.
19 Patents 4,104,323 and 4,141,876.

20 The invention discovery is that polyphenylene oxide
21 copolymers, having low molecular weight and high glass transition
22 temperatures, extend the temperature range of pressure sensitive and
23 hot melt adhesive systems which contain styrenic triblock
24 copolymers. This is a consequence of their compatibilities with the
25 polystyrene domains of the triblock copolymers used in these adhesive
26 applications. Because these adhesive formulations are useful up to
27 the glass transition temperature of the polystyrene domains, blending
28 a high T_g PPO polymer into the polystyrene domains increases the
29 T_g of the glassy domains and consequently increases the useful
30 temperature range of the adhesive. The glass transition temperature
31 range for the PPO resin, 100-165°C, preferably 140-163°C enables hot
32 melt application of the adhesive formulation. Higher T_g PPO resins
33 cannot be hot melt processed unless they are preblended with low
34 molecular weight aromatic resins such as polystyrene as described in
35 U.S. Patent 4,104,323. Furthermore, the lower T_g PPO's of this

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1 invention provide superior adhesive properties compared with the
2 higher T_g PPO's.

3 According to the "Glossary of Terms Used in the Pressure
4 Sensitive Tape Industry", a pressure sensitive adhesive is a material
5 which is aggressively and permanently tacky, adheres without the need
6 of more than finger pressure, exerts a strong holding force, and has
7 sufficient cohesiveness and elasticity that it can be removed from
8 substrates without leaving a residue. A hot melt adhesive, on the
9 other hand, is a 100% nonvolatile thermoplastic material that is
10 heated to a melt and applied to the substrate as a liquid. The hot
11 melt bond forms after the liquid cools and solidifies. Some pressure
12 sensitive adhesives, such as those based on block copolymers, are
13 applied as hot melts, and are referred to as hot melt-pressure
14 sensitive adhesives.

15 Typically, commercial PPO's are derived from the
16 2,6-dimethyl phenol monomer. In accordance with this invention there
17 is described the use of high T_g, PPO copolymers. One advantage of
18 the use of the copolymers is the lower cost of the monomers such as
19 o-cresol as compared with the more expensive 2,6-dimethyl phenol
20 monomer thereby resulting in a lower cost PPO. Further, the use of
21 comonomers yields the low molecular weight PPO resins which are best
22 suited for these applications. The useful glass transition
23 temperature range for these PPO resins ranges from 100-165°C,
24 preferably between 140-163°C. This range, less than that described
25 in U.S. Patents 4,104,323 and 4,141,876, provides superior adhesive
26 service temperature increases while allowing hot melt processibility
27 below 200°C.

28 These low molecular weight polyphenylene oxides improve the
29 high temperature performance of styrenic block copolymers in pressure
30 sensitive adhesive systems. For example, a 7 parts per one hundred
31 rubber (phr) loading of the PPO in a formulation provides about a
32 32°F improvement in the shear adhesion failure temperature (SAFT)
33 with little impact on the pressure sensitive adhesive's tack.

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DETAILED DESCRIPTION OF THE INVENTION

1 In the use of low molecular weight polyphenylene oxides to
2 increase the service temperatures of block copolymer adhesive
3 systems, the upper use temperature of these adhesives is limited to
4 the softening temperature (T_g) of the polystyrene domains. In
5 accordance with this invention, a high T_g PPO with good polystyrene
6 thermodynamic compatibility increases the service temperature when
7 blended into the adhesive formulation.

8 Block copolymers employed in the invention may have
9 geometrical structures, however the invention does not depend on a
10 particular structure, but rather upon the chemical constitution of
11 each of the polymer blocks. Thus, the structures may be linear,
12 radial, or branched so long as each copolymer has at least two
13 polymer endblocks and at least one polymer midblock. Thus the
14 invention contemplates (but is not limited to) the use of
15 configurations such as $(A-B-A)_n$ where n varies from 1 to 20, and
16 preferably from 1 to 3, most preferably 1. Methods for preparation
17 of such polymers are well known in the art. Although the term
18 triblock is used throughout it is to be understood that where
19 applicable the radial and branched blocks are included.

20 The invention applies especially to the use of polymers
21 having the configuration of the following typical species:

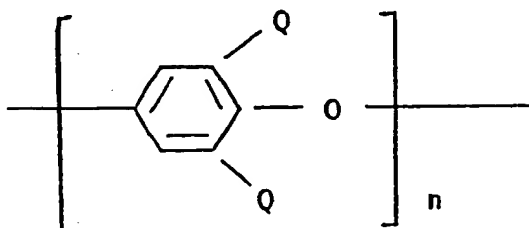
22 polystyrene-polybutadiene-polystyrene (SBS)
23 polystyrene-polyisoprene-polystyrene (SIS)
24 poly(alpha-methylstyrene)-polybutadiene-poly
25 (alpha-methylstyrene) (α MS-B- α MS)
26 poly(alpha-methylstyrene)-polyisoprene-poly
27 (alpha-methylstyrene) (α MS-I- α MS).

28 It is to be understood that both Blocks A and B may be
29 either homopolymer or random copolymer blocks as long as each block
30 predominates in at least one class of the monomers characterizing the
31 blocks as defined. Thus, blocks A may comprise styrene/alpha-
32 methylstyrene copolymer blocks or styrene/butadiene random copolymer
33 blocks as long as the blocks individually predominate in monoalkenyl
34 arenes. The term "monoalkenyl arene" includes styrene and its

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1 analogs and homologs including alpha-methylstyrene and
 2 ring-substituted styrenes, particularly ring-methylated styrenes.
 3 The preferred monoalkenyl arenes are styrene and alpha-methylstyrene,
 4 and styrene is particularly preferred. The blocks B may comprise
 5 homopolymers of butadiene, isoprene, copolymers of butadiene and
 6 isoprene and copolymers of one of these two dienes with monoalkenyl
 7 arene as long as the blocks B predominate in conjugated diene units.
 8 The rubbery midblock of these polymers may be hydrogenated, but
 9 non-hydrogenated midblocks can also be used since excessively high
 10 blending temperatures are not generally required to prepare the
 11 blends of the present inventory. When the monomer employed is
 12 butadiene, it is preferred that between about 35 and about 55 mole
 13 percent of the condensed butadiene units in the butadiene polymer
 14 block, have a 1,2 configuration.

15 Polyphenylene oxides of the invention will have repeating
 16 units represented by the formula:



17 wherein the oxygen ether atom of one unit is connected to the benzene
 18 nucleus of the next adjoining unit, n is a positive integer of from
 19 10 to about 40 thereby providing a MW range of about 1000-5000, and
 20 each Q is a monovalent substituent selected from the group consisting
 21 of hydrogen, halogen, hydrocarbon radicals, hydrocarbonoxy radicals,
 22 and halohydrocarbonoxy radicals having at least two carbon atoms
 23 between the halogen atom and phenyl nucleus. Especially preferred
 24 polyphenylene oxide resins for purposes of the present invention are
 25 those having alkyl substitutions in the two positions ortho to the
 26 oxygen ether atom - i.e. where each Q is alkyl, most preferably,
 27 having from 1 to 4 carbon atoms.

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1 The polyphenylene oxides employed in accordance with the
2 invention, prepared from 2,6-xyleneol and additional comonomers such
3 as o-cresol, allow the cost of the PPO to be materially reduced.
4 Also, since it is necessary to control the extent of polymerization
5 to obtain PPO products of low molecular weights, the use of the
6 comonomers and control of the amount of oxygen admitted to the
7 reaction allows preparation of the low molecular weights necessary to
8 the invention.

9 In general, the low molecular weight polyphenylene oxides
10 are prepared using a cuprous chloride-pyridine catalyst system in
11 chlorobenzene solution. Magnesium sulfate is used to remove moisture
12 from the reactions. The products are isolated by precipitation with
13 a 10% HCl/methanol solution, and are dissolved and reprecipitated to
14 remove any residual traces of catalyst or diphenoquinone side
15 products.

16 PPO yields and glass transition temperatures are controlled
17 by varying the degree of polymerization. This is achieved by
18 changing the reaction time and consequently the amount of oxygen. A
19 longer reaction time permits the formation of higher molecular weight
20 and high T_g products, which, when precipitated, afford higher
21 recoveries.

22 Further control of the molecular weight is provided by the
23 use of o-cresol or other comonomers, which give low degrees of
24 polymerization with the present catalyst system.

25 Polyphenylene oxides of low molecular weight, useful in the
26 invention, also can be prepared according to the Perec article in J.
27 of Polymer Science (vol 25, p 2605) from 4 bromo-2,6-dimethylphenol
28 as monomer (see Example 5).

EXAMPLE 1

29 Cuprous chloride (10g) and pyridine (50ml) are stirred for
30 30 minutes in 500 ml chlorobenzene. o-Cresol (48ml) and anhydrous
31 magnesium sulfate (1.5g) are added and the reaction is stirred for 28
32 hours at room temperature. The insoluble portion of the reaction is
33 filtered away and the resin is precipitated with a 10% HCl/methanol

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1 solution. The resin is isolated by filtration and washed with
2 methanol. The yield is 15g (30%) of a pale orange, brittle solid.
3 The glass transition temperature of the solid is 103°C and H-NMR of
4 the solid shows a 1:1 ratio of aliphatic to aromatic protons.

EXAMPLE 2

5 Cuprous chloride (10g) and pyridine (50ml) are stirred for
6 30 minutes at room temperature in 500 ml chlorobenzene. o-Cresol
7 (25g), 2,6-xyleneol (25g), and anhydrous magnesium sulfate (1.5g) are
8 added and the reaction is stirred for 28 hours. The insoluble
9 portion of the reaction mixture is removed by filtration and the
10 resin is isolated by precipitation with 10% HCl/methanol. The resin
11 is isolated by filtration and redissolved in toluene and precipitated
12 with methanol to remove any residual catalyst or dimeric side
13 products. The yield is 38g (76%) of a pale orange solid. The glass
14 transition temperature is 105°C and H-NMR analysis shows a 5:3 ratio
15 of aliphatic to aromatic protons.

EXAMPLE 3

16 The procedure of Example 2 is followed except that 26.5g of
17 2,6-xyleneol and 26.5 g of o-cresol are used. The reaction is stirred
18 for 48 hours. A 70% yield of a pale orange solid is obtained. The
19 glass transition temperature of the resin is 153°C and H-NMR analysis
20 shows a 9:5 ratio of aliphatic to aromatic protons.

EXAMPLE 4

21 The procedure of Example 1 is followed except that 50g of
22 2,6-xyleneol is used instead of the o-cresol. Also, the resin is
23 dissolved in toluene and precipitated with methanol. A 61% yield of
24 a yellow solid is obtained. The glass transition temperature of the
25 solid is 154°C and H-NMR analysis of the solid shows a 3:1 ratio of
26 aliphatic to aromatic protons.

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EXAMPLE 5

1 4-Bromo-2,6-dimethylphenol (38g) is dissolved in 316 ml 6N
2 NaOH. Ammonium hydrogen sulfate (5.08g) and 316 ml toluene are
3 added, and the mixture is stirred for 2 3/4 hours, whereupon, it is
4 quenched with dilute HCl. The toluene phase is separated and dried
5 with magnesium sulfate, and the polymer is isolated by precipitation
6 with methanol (5.5g). DSC and GPC analyses are performed with the
7 following results: $T_g=163^{\circ}\text{C}$, $M_n=2600$, $M_w/M_n=1.53$.

EXAMPLE 6

8 The procedure of Example 3 was followed except that 75g 2,
9 6-xyleneol, 50 mol pyridine, 900 ml chlorobenzene, and 5g magnesium
10 sulfate were used. The mixture was stirred for 72 hours. The
11 polymer yield was 43.5g, and the glass transition temperature was
12 145°C .

13 In summary, the yields, glass transition temperatures, and
14 product compositions for the PPO products prepared for testing in
15 adhesive formulations are as follows:

		<u>GLASS TRANSITION</u>	<u>YIELD</u>	<u>COMPOSITION</u>
		<u>TEMPERATURE</u>		
16	Example 1	103°C	30%	o-Cresol
17	Example 2	105°C	76%	3:4 Xylenol:o-Cresol
18	Example 3	153°C	70%	1:1 Xylenol:o-Cresol
19	Example 4	154°C	61%	Xylenol
20	Example 5	163°C	24%	Xylenol
21	Example 6	145°C	30%	1:1 Xylenol:o-Cresol

22 PPO product compositions were determined using H-NMR
23 spectroscopy. A ratio of aliphatic protons (1.5-2.5 ppm) to aromatic
24 protons (6-7.4 ppm) indicates the relative amounts of cresol and
25 xyleneol present in the resins. An entirely 2,6-xyleneol product
26 contains a 3:1 ratio of aliphatic to aromatic protons while an
27 entirely o-cresol product contains a 1:1 ratio of aliphatic to
28 aromatic protons.

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1 In the following embodiments, examples and comparisons,
2 these materials were employed:

- 3 ✓ (1) Kraton 1107; a styrene-isoprene-styrene block copolymer from
4 Shell having block molecular weights of about
5 13,000-160,000-13,000.
6 (2) ESCOREZ 1310LC; a C₅ olefin/diolefin tackifying resin from
7 Exxon Chemicals having a ring and ball softening point of
8 95°C.
9 (3) Stereon 840A; a tapered styrene-butadiene-styrene block
10 copolymer from Firestone having Mn of 60,000 and 43 wt %
11 styrene.
12 (4) Zonatac 105L; a limonene/styrene tackifying resin from
13 Arizona Chemicals having a ring and ball softening point of
14 105°C.
15 (5) Shellflex 371; a naphthenic extending oil from Shell.
16 (6) Irganox 1010; an antioxidant from CIBA-Geigy.
17 (7) Noryl; a PPO from General Electric having a Tg of 194°C.

ADHESIVE TESTING WITH SIS FORMULATIONS

18 S-I-S formulations with E-1310LC as tackifier resin were
19 prepared for testing as pressure sensitive adhesives. All PPO
20 products were used at two different levels and the 90° quick stick,
21 180° peel, polyken tack, and shear adhesion failure temperatures were
22 measured for each of the formulations. The formulations were cast
23 from toluene onto mylar, and dried in an oven at 80°C to give a .0015
24 in. coating.

25 The adhesive tests are those commonly employed by the
26 pressure sensitive adhesive industry. In the shear adhesion failure
27 temperature test, a 1"x1" overlap of tape to a stainless steel
28 substrate is made with a 4.5 pound roller. A 1 kg weight is hung
29 from the tape and the assembly is placed in an oven. The temperature
30 is increased at 40°F/hour and the temperature at which the weight
31 drops is recorded as the SAFT. In the polyken tack test, a steel
32 probe contacts the adhesive tape with a specified force for a 1

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1 second dwell time. The force required to break the bond between the
 2 adhesive and the stainless steel probe is measured (g). The 180°
 3 peel test involves placing a length of tape on a stainless steel
 4 plate and laminating it with a 1-pound roller. The force (lb/in)
 5 required to peel the tape at a 180° angle on an Instron is recorded.

6 The results of the adhesive testing are summarized in Table
 7 1.

TABLE 1

8	1-4 Control 1 2 3 4 5-8 5 6 7 8 9											
	Control											
9	KRATON 1107	100	100	100	100	100	100	100	100	100	100	100
10	E-1310LC	150	150	150	150	150	150	150	150	150	150	150
11	PPO Ex. 1	-	7.3	14.7	-	-	-	-	-	-	-	-
12	PPO Ex. 2	-	-	-	7	14	-	-	-	-	-	-
13	PPO Ex. 3	-	-	-	-	-	-	7	14	-	-	-
14	PPO Ex. 4	-	-	-	-	-	-	-	-	7	14	-
15	PPO Ex. 5	-	-	-	-	-	-	-	-	-	-	7
16	Irganox 1010	.2	2	2	2	2	2	2	2	2	2	2
17	90° Quick											
18	Stick											
19	(lbs/in)	2.3	2.3	2.9	2.6	2.6	1.5	2.7	1.9	1.5	1.1	-
20	180° Peel to											
21	SS (lbs/in)	6.4	6.2	6.0	5.9	5.6	4.9	5.1	5.6	4.9	5.3	6.25
22	Polyken Tack											
23	(g)	1000	702	605	737	350	720	603	495	699	518	1480
24	SAFT											
25	(°F)	200	217	220	229	244	204	234	248	237	244	232

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1 It is apparent from Table 1 that the examples representative
2 of the invention have superior SAFT than those of the comparative
3 examples. This indicates that lower T_g PPO resins are also useful
4 in increasing the service temperatures of adhesives. Finally, the
5 tack and peel properties of these adhesives are not adversely
6 affected by the PPO resins as indicated by maintenance of the peel
7 and quick stick values with modest declines in polyken tack.

8 Figure 1 illustrates the adhesive performance findings for
9 use of the PPO product of Example 3 with SIS formulations.

ADHESIVE TESTING WITH SBS FORMULATIONS

10 Stereon 840 (SBS) formulations with a Zonatac 105 Lite/
11 Shellflex 371 tackifying system were prepared for testing as hot melt
12 adhesives. All four PPO products were used at different levels and
13 the results of the 180° peel and shear adhesion failure temperatures
14 are compiled in Table 2.

15 Figure 2 illustrates the superior adhesive performance
16 findings for the use of the PPO product of this invention with SBS
17 formulations.

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TABLE 2

	<u>1-4 Control</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5-8 Control</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9-12 Control</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>
STEREON 840A	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Zonatac 105 Lite	120	120	120	120	120	148	134	120	134	120	148	134	120	134	120
Shellflex 371	30	30	30	30	30	28	28	28	28	28	-	-	-	-	-
PPO Ex. 1	-	5	10	-	-	-	-	-	-	-	-	-	-	-	-
PPO Ex. 2	-	-	-	5	10	-	-	-	-	-	-	-	-	-	-
PPO Ex. 3	-	-	-	-	-	-	14	28	-	-	-	14	28	-	-
PPO Ex. 4	-	-	-	-	-	-	-	-	14	28	-	-	-	14	28
Irganox 1010	2	2	2	2	2	2	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
180° Peel to SS (1bs/in)	4.2	2.5	2.9	2.6	1.5	4.4	3.8	1.8	5.8	0.9	3.2	1.9	1.5	3.0	0.7
SAPT (°F)	160	176	184	193	213	165	197	214	203	216	170	200	220	216	235

TABLE 3: FORMULATION VISCOSITY PROFILE

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
1 Kraton 1107	4g	4g	-	-
2 Stereon 840A	-	-	3.6g	3.6g
3 Escorez 1310LC	6g	6g	-	-
4 Zonatac 105Lite	-	-	5.4g	4.3g
5 PPO Ex. 3	-	0.6g	-	-
6 PPO Ex. 4	-	-	-	1.0g
7 Shellflex 371	-	-	1.0g	1.0g
8 Viscosity (Ps)				
9 180°C	764	710	146	392
10 200°C	280	302	88	173
11 220°C	120	94	57	96

12 The viscosity results indicate that the PPO products of the
 13 invention can be formulated into adhesive formulations for hot
 14 melts without significantly altering the viscosity profile.

15 Stereon 840 (SBS) formulations with a Zonatac 105
 16 Lite/Shellflex 371 tackifying system were prepared for testing as
 17 hot melt adhesives and solvnet cast pressure sensitive adhesives.
 18 For the purpose of comparison of the PPO's of this invention with
 19 the PPO's of the prior art, the formulations were prepared with the
 20 PPO of Example 6 (Tg=145°C) and NORYL (Tg=194°C). For the hot melt
 21 adhesive, viscosity, T-Peel, SAFT and PAFT were evaluated. For the
 22 solvent cast pressure sensitive adhesive, 180° peel and SAFT were
 23 evaluated.

24 The T-Peel test was performed according to the procedure
 25 of ASTM D01876-72, for both aluminum and polyethylene. The shear
 26 adhesion failure temperature (SAFT) was determined as described

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1 above, except that a 500 g weight was used for a 1" x 1" overlap of
2 Kraft paper bonded to Kraft paper. The peel adhesion failure
3 temperature (PAFT) utilized the same geometry as the ASTM D-1876-72
4 T-Peel test except with a 1" x 1" overlap of Kraft paper bonded to
5 Kraft paper. The PAFT evaluation was conducted in an oven with a
6 200 g weight attached. The reported temperature was the
7 temperature at which the bond failed when the oven was ramped at
8 40°F/hour. The 180° peel test was as described above. The results
9 of the adhesive testing are summarized in Table 4.

10 While the invention has focused on the use of certain
11 particular low molecular weight PPO polymers having a T_g of about
12 100°C to about 165°C to improve the upper temperature performances
13 of styrene block copolymer adhesive systems, it is to be understood
14 that a wide range of these polymers are suitable and that the
15 compositions can be dictated by economic considerations. For
16 example, the data show that cresol copolymers exhibited
17 performances comparable to the more expensive xylenol homopolymer.
18 Therefore, many monomer combinations based on cresylic acids and
19 phenol methylation products can be used without departing from the
20 spirit and scope of the use of low molecular weight PPO polymers
21 for high temperature applications in pressure sensitive and hot
22 melt adhesive systems.

TABLE 4: PPO T_g COMPARISON

		<u>Hot Melt Adhesive</u>		<u>Solvent Cast PSA (from toluene)</u>	
		<u>1</u>	<u>2</u>	<u>1</u>	<u>2</u>
1	STEREON 840A	100	100	100	100
2	Zonatac 105 Lite	120	120	120	120
3	Shellflex 371	38.6	38.6	38.6	38.6
4	PPO Ex. 6				
5	(T _g =145°C)	38.6	--	38.6	--
6	NORYL PPO				
7	(T _g =194°C)	--	38.6	--	38.6
8	Brookfield Viscosity				
9	180°C	24,450 cps	---		
10	200°C	11,500 cps	---		
11	T-Peel (lb/in.)				
12	Al/Al	7.1	---		
13	PE/PE	0.1	---		
14	SAFT (°F)				
15	1" x 1" x 500g				
16	Kraft/Kraft	200	---		
17	PAFT (°F)				
18	1" x 1" x 100g				
19	Kraft/Kraft	212	---		
20	180°Peel (lb/in.)				
21	SS			2.5	0.2
22	SAFT (°F)				
23	1" x 1" x 1000g			213	97
24	*NORYL PPO immiscible up to 220°C				

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1 The most remarkable feature of the data presented in Table 4
2 is that the NORYL (tg=194°C) could not be hot melt blended at
3 temperatures up to 220°C, in contrast to the low Tg (145°C) PPO of
4 example 6. Furthermore, the adhesive properties of the lower Tg PPO
5 of Example 6 formulations are superior to properties achieved with
6 the higher Tg NORYL resin formulations. These data demonstrate a
7 clear advantage in processability and in adhesive performance for the
8 low Tg PPO compositions of this invention versus the higher Tg PPO
9 resins taught in the prior art.

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CLAIMS:

1. An adhesive composition having improved shear adhesion failure temperatures (SAFT) comprising:

(a) 100 phr of a block copolymer having at least two monoalkenyl arene polymer endblocks A and at least one elastomeric conjugated-diene midblock B, said blocks A comprising 8-55% by weight of the block copolymer;

(b) about 50 to about 200 phr of a tackifying resin compatible with block B; and

(c) about 5 to about 50 phr of a low molecular weight polyphenylene oxide polymer, having a molecular weight (M_{vis}) between about 1000 and about 5,000, and a T_g of about 100°-165°C.

2. The composition of claim 1 wherein the block polymer is a triblock.

3. The composition of claim 1, wherein the polyphenylene oxide polymer has a T_g of about 140°-163°C.

4. The composition of claim 2, wherein the triblock copolymer comprises styrene endblocks and a polyisoprene rubbery midblock.

5. The composition of claim 2, wherein the triblock copolymer comprises styrene endblocks and a butadiene rubbery midblock.

6. The composition of claim 1, wherein the block copolymer is a triblock copolymer having styrene- α -methylstyrene endblocks and a polyisoprene rubbery midblock.

7. The composition of claim 3, wherein the block copolymer is a triblock copolymer having styrene endblocks and a polyisoprene rubbery midblock.

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8. The composition of claim 3, wherein the block copolymer is a triblock copolymer having styrene endblocks and a butadiene rubbery midblock.

9. The composition of claim 3, wherein the block copolymer is a triblock copolymer having styrene-alpha-methylstyrene endblocks and a polyisoprene rubbery midblock.

10. An adhesive tape comprising the adhesive composition of claim 1.

11. A substrate coated with the adhesive composition of claim 1.

12. The composition of claim 4, wherein the block copolymer is hydrogenated.

13. The composition of claim 7, wherein the block copolymer is hydrogenated.

14. The substrate of claim 12, wherein the substrate is metallic.

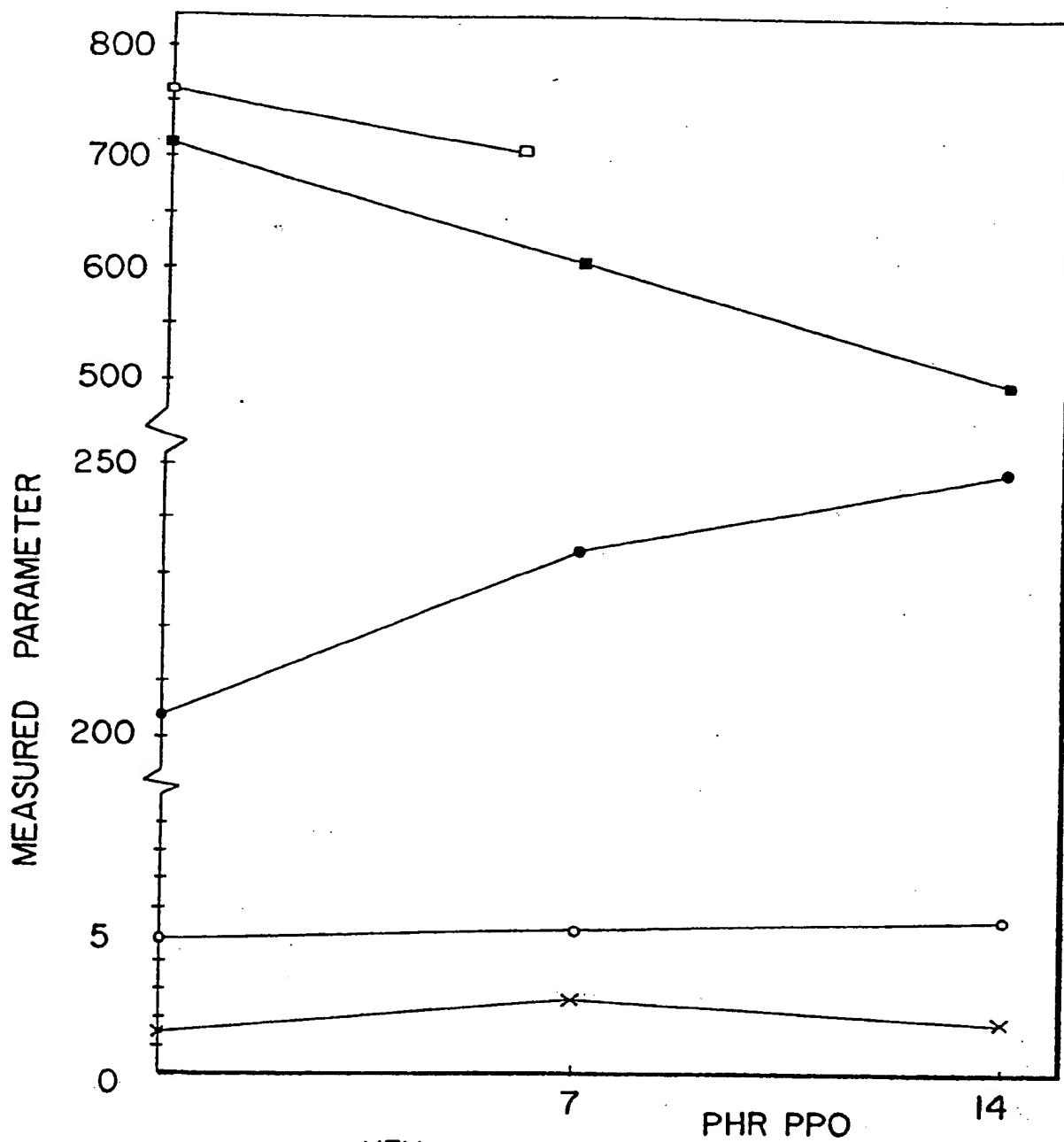
15. A hot melt adhesive comprising the composition of claim 1.

16. A pressure sensitive adhesive comprising the composition of claim 1.

17. A hot melt pressure sensitive adhesive comprising the composition of claim 1.

Fig. 1

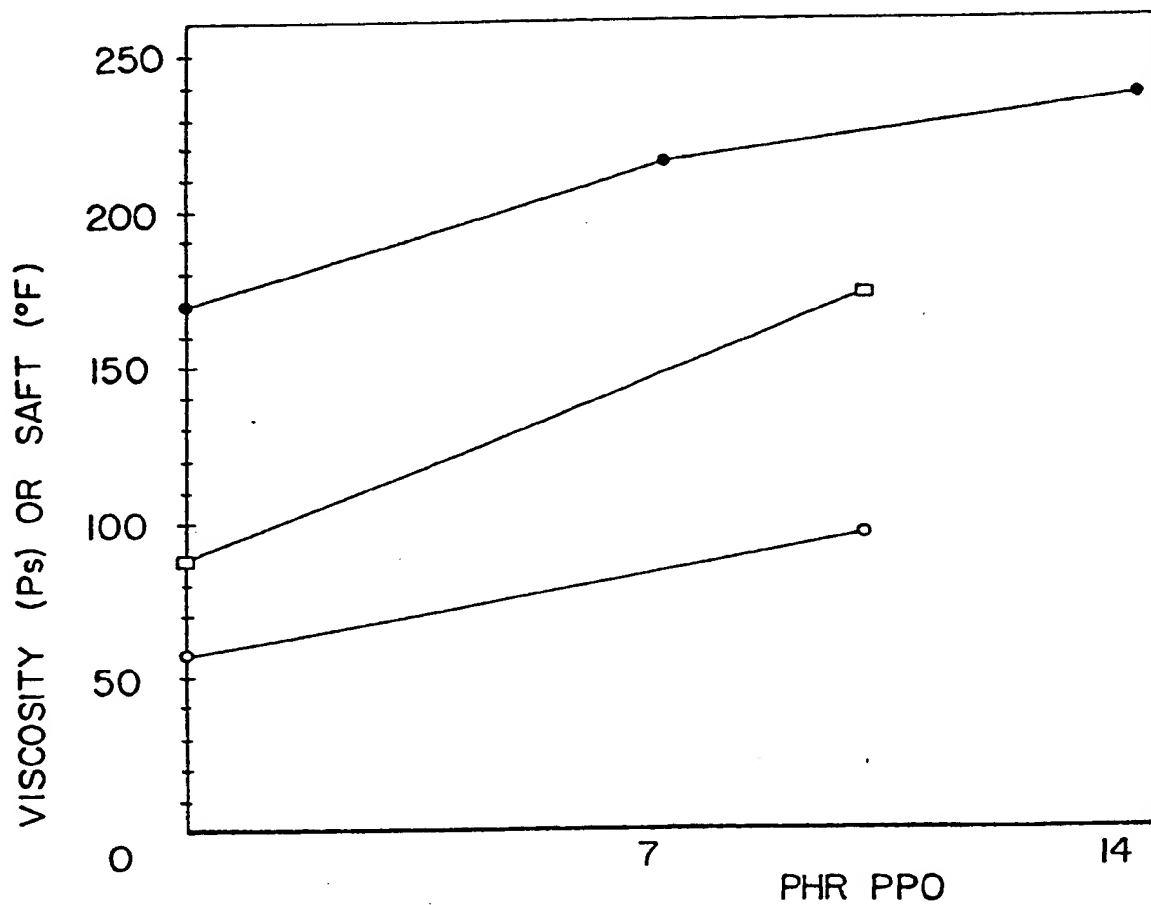
GRAPH 1: SIS/ EXAMPLE 3 PPO

**KEY:**

- VISCOSITY (Ps)
- Polyken Tack (g)
- SAFT (°F)
- 180° Peel (SS lbs/in)
- × 90° Quick Stick (lbs/in)

Fig. 2

GRAPH: 2 SBS/EXAMPLE 3 PPO

KEY:

- SAFT (°F)
- Viscosity (Ps) at 200° C
- Viscosity (Ps) at 220° C

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/02948

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 09 J 153/02											
II. FIELDS SEARCHED <div style="display: flex; justify-content: space-between; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;"> Classification System Minimum Documentation Searched ⁷ </div> <div style="display: flex; justify-content: space-between; border-bottom: 1px solid black; margin: 5px 0;"> IPC⁵ Classification Symbols </div> <div style="display: flex; justify-content: space-between; margin: 5px 0;"> IPC⁵ C 09 J, C 08 L </div> <div style="border-top: 1px solid black; padding-top: 5px; margin-top: 10px;"> Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸ </div>											
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <thead> <tr> <th style="width: 10%;">Category ¹⁰</th> <th style="width: 70%;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;"> EP, A, 0001306 (SHELL) 4 April 1979 see claims (cited in the application) <div style="text-align: center;">--</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">Y</td> <td style="padding: 5px;"> DE, A, 2222230 (ASAHI DOW) 15 November 1973 see claims <div style="text-align: center;">-----</div> </td> <td style="text-align: center; vertical-align: top; padding: 5px;">1-17</td> </tr> </tbody> </table>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	Y	EP, A, 0001306 (SHELL) 4 April 1979 see claims (cited in the application) <div style="text-align: center;">--</div>	1-17	Y	DE, A, 2222230 (ASAHI DOW) 15 November 1973 see claims <div style="text-align: center;">-----</div>	1-17
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<div style="display: flex; justify-content: space-between; font-size: 0.8em;"> <div style="width: 48%;"> <p>¹⁴ Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>											
IV. CERTIFICATION <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of the Actual Completion of the International Search 11th September 1990 </td> <td style="width: 50%; padding: 5px; vertical-align: top;"> Date of Mailing of this International Search Report <div style="text-align: right; font-weight: bold;">11. 10. 90</div> </td> </tr> <tr> <td style="width: 50%; padding: 5px; vertical-align: top;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="width: 50%; padding: 5px; vertical-align: top;"> Signature of Authorized Officer <div style="text-align: right;"> Natalie Weinberg </div> </td> </tr> </table>			Date of the Actual Completion of the International Search 11th September 1990	Date of Mailing of this International Search Report <div style="text-align: right; font-weight: bold;">11. 10. 90</div>	International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: right;"> Natalie Weinberg </div>					
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9002948
SA 37881

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 02/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0001306	04-04-79	US-A- 4141876	27-02-79
		AT-B- 362480	25-05-81
		AU-B- 517163	09-07-81
		AU-A- 4005478	27-03-80
		CA-A- 1133159	05-10-82
		JP-A, B, C54056636	07-05-79
DE-A- 2222230	15-11-73	FR-A, B 2182695	14-12-73
		GB-A- 1393728	14-05-75
		NL-A- 7206025	06-11-73